Stacking Entropy of Hard Sphere Crystals

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Abstract

Classical hard spheres crystallize at equilibrium at high enough density. Crystals made up of stackings of 2-dimensional hexagonal close-packed layers (e.g. fcc , hcp , etc.) differ in entropy by only about $10^{-3}k_B$ per sphere (all configurations are degenerate in energy). To readily resolve and study these small entropy differences, we have implemented two different multicanonical Monte Carlo algorithms that allow direct equilibration between crystals with different stacking sequences. Recent work had demonstrated that the fcc stacking has higher entropy than the hcp stacking. We have studied other stackings to demonstrate that the fcc stacking does indeed have the highest entropy of *all* possible stackings. The entropic interactions we could detect involve three, four and (although with less statistical certainty) five consecutive layers of spheres. These interlayer entropic interactions fall off in strength with increasing distance, as expected; this fall-off appears to be much slower near the melting density than at the maximum (close-packing) density. At maximum density the entropy difference between fcc and hcp stackings is $0.00115 \pm 0.00004\, k_B$ per sphere, which is roughly 30% higher than the same quantity measured near the melting transition.

1 Introduction

The question of which crystalline stacking of hard spheres near close packing is thermodynamically stable is a long standing one. The interest is partly due to the extreme anharmonicity of hard core interactions and partly due to the *fcc-hcp* phase transition in solid helium [1]. This problem is difficult both experimentally and theoretically. Experimentally, classical hard spheres are approximated by spherical colloidal particles with interactions whose ranges are very short compared to their radius. Deviations from ideal hard spheres are due to polydispersity of the spheres, and due to interactions. The van der Waals interaction can be reduced by matching the dielectric coefficients of the particles and the solvent [3, 4]. Since, for ideal hard spheres, the free energy differences between the different stackings are very small, as we will see, one would expect the equilibration time to be very long. Most studies have seen a random stacking pattern. However, some experiments have reported that the observed random stacking patterns in slowly-grown or well-annealed colloidal crystals are biassed more towards *fcc* rather than *hcp* stacking [2].

The free energy difference between different classical hard sphere crystals at fixed volume is only due to the entropy difference, since the energy is the same for all allowed configurations. The numerical work, before the present paper, had only looked at the *hcp* and *fcc* stackings. The first studies calculated pressure using molecular dynamics simulations [5] and then obtained entropies by integrating the pressure *vs.* volume along reversible paths from states with known entropy [6, 7, 8, 9]. These studies were not able to detect the entropy difference between *fcc* and *hcp* crystals. Later, Frenkel and Ladd [10] instead integrated along a path connecting the hard sphere model to Einstein crystals of the same lattice structure, by adding to the model ideal springs tethering each ball to its lattice site. In this approach they integrate the derivative of free energy with respect to the spring constant. They came up with the bounds on the entropy difference per sphere: $-0.001 < \Delta s^* < 0.002$ in units of k_B, where $\Delta s^* \equiv s_{fcc} - s_{hcp}$.

Recently, Bolhuis, Frenkel and the present authors used both a new implementation of the multicanonical Monte Carlo (MCMC) method [14, 15], as well as the Einstein crystal method to reduce the statistical errors down to the $10^{-4}k_B$ per sphere level. This allowed us to accurately resolve the entropy difference of roughly $10^{-3}k_B$ per sphere between *fcc* and *hcp* crystals, with the *fcc* crystal having the higher entropy. [12] This quantitatively corrected

the recent pressure-integration study of Woodcock [11], confirming his result that the fcc crystal has higher entropy. More recently, Bruce *et al.* have found a superior implementation of the multicanonical method for this problem, reducing the statistical error in Δs^* down to near the $10^{-5}k_B$ level [13]. The various results for Δs^* are summarized in Table 1. It is clear from the table that MCMC is able to obtain substantially smaller statistical errors for this problem, compared to the more conventional integration methods.

The reason why integration methods were used initially was that it did not appear possible for the hard-sphere system to equilibrate between the fcc and hcp crystal structures, due to the very large, or even infinite, free energy barrier separating them. This was certainly true for standard molecular dynamics or Monte Carlo methods. However, the MCMC method, the implementations of which we will summarize below, is designed precisely to eliminate such large free energy barriers and allow equilibration between very different states. This permits a direct measurement of the relative entropies of the two states simply by comparing the probabilities of their occurrences in a single simulation.

Since only the hcp and fcc crystals had been examined in previous work, we have also looked at other stackings of hexagonally close packed planes of spheres to make certain that neglecting the other possible stackings was reasonable. The entropy differences between the stackings can be described as due to interactions between layers. We have been able to detect the entropic interaction between a given layer and its nearby layers that are two, three, and possibly even four layers away. These interactions are all of the sign that favors the fcc stacking, so we confirm, as is no surprise, that the fcc stacking has higher entropy than *all* other stackings, not just higher than hcp . At the maximum packing density, we find that the interaction with the third-neighbor layer is roughly an order of magnitude smaller than that with the second-neighbor layer, as seems quite reasonable. For lower density, near the melting transition, the fall-off of these entropic interactions with distance appears to be much slower, presumably reflecting the larger fluctuations of the individual sphere positions.

For any given stacking, the entropy varies as a function of any homogeneous lattice deformation at *constant* volume fraction. For the fcc stacking, the undeformed lattice has cubic symmetry, so must by symmetry be a stationary point of the entropy vs. deformation, and it is the maximum. For the other stackings, there is no such symmetry, and the maximum entropy may be obtained for a deformation where the expansion of the lattice away

from close-packing is not isotropic. We have looked for this possible effect in the *hcp* stacking by measuring the entropy vs. the uniaxial lattice deformation (the c/a ratio). If there is an anisotropy, we were unable to detect it. If there is an entropy difference between the highest entropy state and the isotropically-expanded state for the *hcp* stacking, this difference is less than $10^{-5}k_B$ per sphere, so is well below the statistical errors in our comparisons to the other stackings.

Another issue that arises in simulating hard-sphere crystals is whether collisions between spheres that are not nearest-neighbors can be neglected. It is certainly more convenient to make the approximation of including the hard-sphere interaction only between nearest-neighbors. Of course this approximation is terrible in the liquid phase, but we have found that it is actually quite good in the solid phase even at the melting density. There we detected no difference in Δs^* between the model where only nearest-neighbor spheres interact and the model where second-neighbors also interact, indicating that the difference is also smaller than our statistical errors when comparing the entropies of different stackings. It is usually not clear in the literature whether or not further neighbor interactions have been taken into account. This result of ours shows that it doesn't matter within the solid phase at the presently available resolution of the entropy.

2 Model

The model we study is hard spheres: classical monodisperse spheres that are forbidden to overlap. All permitted configurations (with no overlaps between spheres) have the same energy, which we may set as zero energy. At high enough density this system crystallizes at equilibrium, and it is this crystalline equilibrium phase that we study here. Some of our results are for the maximum possible, or close-packed density, which means the system is being treated perturbatively to lowest order in the difference between the density and the close-packed density. In this limit the system is equivalent to a simpler system of aligned, hard dodecahedra [9].

We consider close-packed crystal structures that consist of planes of hexagonally close-packed (in 2-dimensions) spheres stacked up in the vertical direction. As is standard in discussing close-packed crystals, the stacking sequence can be denoted by a sequence of the letters A, B and C, with nearest-neighbor layers in the sequence always having different letters. Any

global permutation on the letters in the sequence simply represents a rotation, reflection or translation of the structure, so will not change the entropy. ABCABCA... is a sequence that represents the fcc stacking, while ABABABA... represents the hcp stacking. To fully remove the degeneracy associated with the permutations, we may assign a Ising-like spin σ_i to each layer i based on the local stacking sequence of that layer and its nearest-neighbor layers immediately above and below it. If that local stacking matches the fcc pattern (e.g., ABC), $\sigma_i = +1$, while $\sigma_i = -1$ if it instead matches the hcp pattern (e.g., ABA). For the three layers being compared, all local stacking patterns are equivalent to one of these two under permutations of the labels A, B and C. This maps each stacking sequence on to a spin pattern of a one-dimensional Ising model.

The entropy of a given stacking is a function of the stacking sequence, which is described by the spins σ_i. It is reasonable to expect that the shortest-range entropic interactions are the largest, so the total entropy may be expanded as

$$S = Ans_0 + Ah \sum_{i=1}^{n} \sigma_i + AJ \sum_{i=1}^{n} \sigma_i\sigma_{i+1} + AJ' \sum_{i=1}^{n} \sigma_i\sigma_{i+2} + Ah' \sum_{i=1}^{n} \sigma_i\sigma_{i+1}\sigma_{i+2} + \cdots, \tag{1}$$

for a stack of n layers containing A spheres per layer. We have periodic boundary conditions so $\sigma_{n+1} = \sigma_1$, etc. The bulk of the entropy is independent of the stacking sequence and given by s_0 per sphere; s_0 is strongly density-dependent. The shortest-range entropic interaction is h, which involves the sequence over three consecutive layers of spheres; this is the shortest sequence that can have distinct stackings. This term is the magnetic field in the corresponding one-dimensional Ising model. The next term is the interaction J between adjacent spins, and arises from the entropic interactions among four consecutive layers of spheres that are not already captured by the first term h. We find, as is reasonable, that $J < h$. The next longer-range interactions (h' and J') that involve five consecutive layers are also displayed above; only in one case (h' for density near melting) could we detect these interactions in our simulations at a level that may be statistically significant.

The intuition behind this model is that the entropy of a sphere is mostly determined by how it is caged by its nearest neighbors and to a progressively lesser extent by the further neighbors. The interaction parameters do depend on the density. We find that, in units of $10^{-5}k_B$ per sphere, the entropic interactions that we could detect change from $(h, J) \cong (55, 6)$ at the

highest density (close-packing) to $(h, J, h') \cong (37, 18, 9)$ at the lowest density that the equilibrium crystal can have before it melts (at roughly 74% of the close-packed density). All detected interactions are of the sign such that the fcc stacking has the largest entropy.

3 Multicanonical Monte Carlo Method

To make direct comparisons of the entropies of hard-sphere crystals with different stacking sequences, we want an algorithm that will produce direct equilibration between the two sequences. Then the entropy difference is simply the logarithm of the ratio of the equilibrium probabilities of the system exhibiting the two sequences in question. Of course, near close-packing the hard spheres in a physically realistic molecular dynamics or Monte Carlo simulation are strongly trapped by their neighbors, so the stacking pattern will not change in any reasonable time scale. The multicanonical method [14, 15] was invented to allow systems to transform at equilibrium between states that are separated by a high free energy barrier. This method has been generalized and applied to this hard-sphere crystal problem in two ways, which we describe next.

In both implementations the position of sphere i is given as $\mathbf{r_i} = \mathbf{R_i} + \mathbf{u_i}$, where $\mathbf{R_i}$ is the ideal reference lattice position in the absence of fluctuations and $\mathbf{u_i}$ is the displacement of sphere i away from that reference position. The algorithms both have Monte Carlo moves that change the reference lattice without changing the displacements $\mathbf{u_i}$, as well as more standard moves that move individual spheres without changing the reference lattice. We describe the shear implementation first; this method we developed and used to obtain our first results [12]. However, Bruce, *et al.* [13] subsequently developed the simpler overlap implementation, which we find is computationally more efficient and easier to program, so we used it for all of our more recent simulations.

3.1 Shear Implementation

In the shear implementation we used an equally-spaced sequence of ideal reference lattices, $\mathbf{R_i}(\lambda)$, labelled by an index, $\lambda = 0, 1, 2, ..., h$, that linearly interpolate between the two stackings of interest, which are the beginning

($\lambda = 0$) and the end ($\lambda = h$) of that sequence. Thus we have

$$h\mathbf{R_i}(\lambda) = (h - \lambda)\mathbf{R_i}(0) + \lambda\mathbf{R_i}(h). \tag{2}$$

This produces a λ-dependent relative shear between each pair of adjacent layers whose local stacking pattern changes. The reference sites in the intermediate lattices ($0 < \lambda < h$) are not all equally spaced, and generally some are too close together for the hard spheres to fit without touching. In the original model, two spheres are assumed to touch if their separation, $|\mathbf{r_i} - \mathbf{r_j}|$, is less than d, the diameter of a sphere, and this must remain true for the two stackings of interest, which are represented by $\lambda = 0$ and h. For the intermediate lattices, on the other hand, we allow the distance of contact, $d_{ij}(\lambda)$ to be either larger or smaller for each pair of nearby spheres in adjacent layers whose relative reference position, $\mathbf{R_i} - \mathbf{R_j}$, changes with changing λ. We attempt, using feedback, to choose these $d_{ij}(\lambda)$ so that the entropy is a monotonic function of λ and the average displacements, $< \mathbf{u_i} >$ vanish for all i and λ. Note that the pairwise interactions are different for each interpolation point, λ. This is different from the original MCMC method [14, 15], where the Gibbs distribution is multiplied by a λ-dependent (but otherwise configuration-independent) reweighting factor, in order to make the free energy monotonic between the two states of interest, thus eliminating the free energy barrier.

To start simulating one has to choose how many interpolation points to use, h, and values for the $d_{ij}(\lambda)$. There are two types of moves. One is a single sphere move, changing one of the displacements $\mathbf{u_i}$. The other is a λ-move that increases or decreases λ by one without changing any of the sphere displacements. Any attempted move of either type is accepted if it does not result in any contact between spheres. The entropies and average displacements, as well as the acceptance rates of the moves are measured. Based on these results h is adjusted to attempt to maximize the rate of equilibration between the two stackings of interest, and the $d_{ij}(\lambda)$ are adjusted to attempt to make the entropy monotonic and eliminate the average displacements. If this feedback is successful, we then measure the relative entropy of the two stackings.

We succeeded in getting this procedure to work for comparing the fcc and hcp stackings for lattices of size up to 8^3. However, the difficulty of getting the feedback to converge appeared to be increasing strongly with lattice size. Typically, "bottlenecks" would form between the two stackings of interest where the λ-move acceptance rate was very small or zero, preventing

equilibration, and the attempts at eliminating these bottlenecks through the feedback were time-consuming and not always succesful. However, we were able to obtain the entropy difference between the fcc and hcp stackings to within statistical errors of roughly $10^{-4}k_B$ per sphere [12], as is summarized in Table 1. Then we learned of the much more staightforward overlap implementation of MCMC for this problem reported by Bruce, *et al.* [13], which we discuss next.

3.2 Overlap Implementation

The overlap implementation of MCMC [13] uses only two reference lattices, which are the two different stackings whose entropy we are comparing. Let us call these two reference lattices α and β. Again there are standard single-sphere moves and changes of the reference lattice. For any reasonable sized lattice, the move that changes reference lattices will be rejected due to sphere overlaps for all but an infinitesimal fraction of the sphere configurations. What is needed is to bias the simulation towards those rare sphere configurations that allow the stacking to be changed.

To do this, Bruce *et al.* [13] introduce the overlap order parameter

$$\mathcal{M}(\{\vec{u}\}) \equiv M(\{\vec{u}\},\alpha) - M(\{\vec{u}\},\beta) \tag{3}$$

where $M(\{\vec{u}\},\gamma)$ is the number of pairs of spheres that overlap in the configuration $\{\vec{u}\}$ for stacking γ. For any allowed configuration with stacking γ, $M(\{\vec{u}\},\gamma) = 0$, but for configurations of the other stacking, usually $M(\{\vec{u}\},\gamma) > 0$. To have the change of stacking be an allowed move, we need $\mathcal{M}(\{\vec{u}\}) = 0$, so no overlaps are produced by the move that changes the reference lattice.

The overlap multicanonical simulation samples the biassed, but unnormalized, distribution

$$P(\{\vec{u}\},\gamma \mid \{\eta\}) \equiv P(\{\vec{u}\},\gamma)\; e^{\eta(\mathcal{M}(\{\vec{u}\}))}, \tag{4}$$

where $P(\{\vec{u}\},\gamma)$ for (unbiassed) hard spheres is simply a constant for all allowed sphere configurations in stacking γ, and is zero otherwise. The weights $\{\eta\}$ are chosen to eliminate the free energy barrier separating the two stackings, thus allowing equilibration between them.

Let $P(\mathcal{M})$ be the equilibrium, normalized, unbiassed ($\eta(\mathcal{M}) = 0$ for all $\mathcal{M}$) probability distribution of the overlap, assuming the system does fully

equilibrate between the two stackings. Then the probability of being in stacking α is

$$P_\alpha = \frac{P(0)}{2} + \sum_{\mathcal{M}<0} P(\mathcal{M}), \tag{5}$$

and the entropy difference we are interested in is

$$S_\alpha - S_\beta = k_B \ln\left(\frac{P_\alpha}{1 - P_\alpha} \right). \tag{6}$$

$P(\mathcal{M})$ has a local minimum at $\mathcal{M} = 0$ and local maxima at positive and negative $\mathcal{M}$ that represent the most probable overlaps for the two different stackings. The weights $\eta(\mathcal{M})$ are chosen to be nonzero only between these two local maxima of $P(\mathcal{M})$. The unnormalized, biassed probability distribution for $\mathcal{M}$ is

$$P(\mathcal{M} \mid \{\eta\}) = P(\mathcal{M})\ e^{\eta(\mathcal{M})}. \tag{7}$$

We choose the weights $\{\eta\}$ so that $P(\mathcal{M} \mid \{\eta\})$ is linear in $\mathcal{M}$ between the maxima of $P(\mathcal{M})$. A simulation with a given set of weights produces estimates of $P(\mathcal{M})$ and also a new estimate of what the appropriate weights are to achieve this linearity. These new weights are then used for the next, longer simulation if the statistical errors have not yet been reduced down to the desired level. This procedure straightforwardly and effectively eliminates the free energy barrier between the two stackings and allows an accurate measurement of the entropy difference.

The overlap implementation of MCMC does not suffer from the tendency to form "bottlenecks" that slowed down the equilibration between the two stackings in our shear implementation of MCMC. We used the overlap method to obtain most of the data reported in this paper. Where we compared the two implementations the measured entropy differences were, of course, the same.

3.3 Boundary Conditions

Suppose one stacks N_3 planes of 2-dimensionally (hexagonally) close-packed spheres to form an arbitrary stacking. Each plane has $N_1 \times N_2$ spheres [1],

[1] We always choose $N_1 = N_2$ to preserve the hexagonal in-plane symmetry

N_1 in the i-direction and N_2 in the j-direction. The i-direction is chosen to coincide the the x-direction and the j-direction is chosen at 60° anti-clockwise from the x-direction looking from above. i and j are the two basis directions of the 2-dimensional close packing. Each site has coordinate (i, j) in-plane, $i = 0, 1, \ldots, N_1 - 1$ and $j = 0, 1, \ldots, N_2 - 1$.

Any stacking can be formed by fixing the position of the (i, j, k) reference site (in layer k) relative to the *same* site $(i, j, k \pm 1)$ in the nearest layers. Define $\vec{\Sigma}_k = \vec{R}(i, j, k+1) - \vec{R}(i, j, k)$, where $\vec{R}$ are the reference sites. We take our unit length to be the lattice spacing so $|\vec{\Sigma}_k| = 1$. We use

$$\vec{\Sigma}_k = \begin{cases} \vec{\Sigma}_+ \equiv (\frac{1}{2}, \frac{1}{\sqrt{12}}, \sqrt{\frac{2}{3}}) & \text{if from layer } k \text{ to layer } k+1 \text{ is a} \\ & \quad \text{forward permutation of } ABC, \\ \vec{\Sigma}_- \equiv (\frac{1}{2}, -\frac{1}{\sqrt{12}}, \sqrt{\frac{2}{3}}) & \text{if from layer } k \text{ to layer } k+1 \text{ is a} \\ & \quad \text{backward permutation of } ABC. \end{cases} \tag{8}$$

Taking $\vec{\Sigma}_k = \vec{\Sigma}_+$ for all k gives an fcc stacking. For the *hcp* stacking $\vec{\Sigma}_k = \vec{\Sigma}_+$ for k even and $\vec{\Sigma}_k = \vec{\Sigma}_-$ for k odd (or *vice versa*).

All simulations are done with periodic BC which is implemented in the usual way:

$$\begin{aligned} \text{sphere at site } (i, j, k) &= \text{sphere at site } (i + N_1, j, k) \\ &= \text{sphere at site } (i, j + N_2, k) \\ &= \text{sphere at site } (i, j, k + N_3), \end{aligned}$$

so $\vec{\Sigma}_k = \vec{\Sigma}_{k+N_3}$. Our implementation of periodic BC allows any N_3 which is a multiple of both of the periods of the $\vec{\Sigma}_k$ patterns of the two stackings in a given simulation. For example, the period for fcc is one layer, while that for *hcp* is two layers, so N_3 can be any even number when we compare fcc and *hcp* entropies.

4 Results

Our results for entropy differences between different stackings at both close-packing ($\rho/\rho_{cp} = 1$) and near melting ($\rho/\rho_{cp} = 0.739$) for different system sizes are summarized in Table 2. A statistically significant finite-size effect was detected only for the smallest size 4^3. Based on this, we assume that the

finite-size effect is negligible for sizes 8^3 and larger, and we use those data for calculating the values of the entropic interactions using our Eq.1.

At close packing we fit, using the results of $N = 8^3, 9^3,$ and 10^3 and the various different stackings, first letting all four parameters $\{h, J, J', h'\}$ vary, and then setting $h' = J' = 0$ and only varying $\{h, J\}$. In the former case we obtain $h = 54.6 \pm 2.8, J = 6.1 \pm 1.6, J' = -0.3 \pm 1.1$ and $h' = 3.4 \pm 2.7$ in units of $10^{-5}k_B$ with $\chi^2/(df = 3) = 1.5$ and for the $h' = J' = 0$ fits: $h = 57.2 \pm 2.1$ and $J = 6.0 \pm 2.2$ with $\chi^2/(df = 5) = 1.9$. We can see that the first fit with J' and h' allowed to vary gives values of them consistent with zero. Comparing the two fits we also see that the inclusion of these two longer-range interactions in the fit does not significantly perturb the values of the shorter-range interactions h and J. We therefore conclude that our data can be explained using the model with *only* h and J non-zero. Indeed, J' and h' not being important is consistent with the small system size $N = 8^3$ being close to the thermodynamic limit. The signs of the non-zero interactions all favor fcc stacking, therefore fcc has higher entropy than all other stackings, consistent with experiment[2]. Notice that $h >> J >> J', h'$ shows that the entropic interactions decrease rapidly as their range increases.

Similar fits of our data at a density ($\rho/\rho_{cp} = 0.739$) near melting yield $h = 36.9 \pm 3.1$, $J = 18.2 \pm 3.0$, $J' = 2.5 \pm 2.2$ and $h' = 8.8 \pm 2.8$ with $\chi^2/(df = 2) = 0.2$. Thus it appears that the entropic interactions decrease in relative magnitude with distance much more slowly at this lower density than they do near close-packing, which is perhaps expected, given the larger free volume which allows the spheres to make larger excursions away from their ideal lattice positions. Again, the interactions are all of the sign that favor the fcc stacking. Our detection of h' is only at the three standard deviation level, so has a small chance of being just a statistical fluctuation in the data. However, if we fit assuming $h' = J' = 0$ the quality of the fit declines strongly, giving $h = 43.2 \pm 3.7$ and $J = 17.3 \pm 3.8$ with $\chi^2/(df = 4) = 5.4$.

For a general stacking pattern, the expansion as the density is reduced from close-packing need not be isotropic. For the fcc stacking it must, by the cubic symmetry, but for the other stackings, the expansion along the direction normal to the layers can be different from that along the directions parallel to the layers. We have tested for this by allowing the ratio of these two expansions to vary in a simple simulation of the *hcp* stacking at close-packing, measuring the entropy *vs.* the ratio, and fitting to find the ratio that maximizes the entropy. We find that this optimal ratio is within ± 0.002 of isotropic, and the entropy difference between isotropic expansion and the

optimal expansion ratio is no more than $10^{-5}k_B$ per sphere, so is smaller than the statistical uncertainties in our simulations. Because of this we have always assumed isotropic expansion in the the entropy comparisons we have made.

The issue of further neighbor interactions arises for $\rho/\rho_{cp} < 1$. At close-packing it suffices to test only for collisions between nearest-neighbor spheres because further neighbors cannot touch. Not testing for further-neighbor collisions speeds up the computer program. As the density is reduced can we keep this approximation? For a model that includes only nearest-neighbor interactions between spheres, the crystal is actually only metastable: once a sphere "escapes" from the cage of its nearest-neighbors it wanders freely. We find that for densities at or above the melting density, the rate of these "escapes" is very low, allowing a good measurement of the entropy of the (now metastable) crystal. We have also measured the entropy differences between the model with only nearest-neighbor interactions and the otherwise identical model with nearest and next-nearest-neighbor interactions, $S_n - S_{nn}$, near melting (see Table 3). Of course, adding the extra interactions does reduce the entropy a little (roughly $8 \times 10^{-5}k_B$ per sphere), but this reduction is the same, within errors, for both fcc and hcp stackings. Thus we conclude that any systematic error in our entropy comparisons due to using only nearest-neighbor interactions are smaller than the statistical errors. Therefore, we have used the faster nearest-neighbor only model in most of our simulations near the melting density.

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ρ/ρ_{cp}	N	$10^5 \times \Delta s^*/k_B$		method	ref.
0.736	12000	230	(100)	pressure integration	[11]
0.736	12096	87	(20)	Einstein crystal	[12]
0.7778	5832	86	(3)	MCMC, overlap implementation	[13]
1.00	1000	113	(4)	MCMC, overlap implementation	present
1.00	512	110	(20)	MCMC, shear implementation	present
0.731	512	85	(10)	MCMC, shear implementation	present

Table 1: Recent results of *fcc-hcp* simulations for various densities (scaled by the close-packed density ρ_{cp}). N is the number of spheres in the samples simulated. The entropy difference per sphere is Δs^*, with the statistical errors in parenthesis. (*fcc* has higher entropy.) Please note that the errors are particularly small for the overlap implementation of MCMC developed by Bruce, *et al.*

ρ/ρ_{cp}	N	Δs			$10^5 \times \Delta s/k_B$	
1	4^3	$s_+ - s_-$	=	$2h + 2h'$	91	(5)
1	6^3	$s_+ - s_-$	=	$2h + 2h'$	107	(4)
1	8^3	$s_+ - s_-$	=	$2h + 2h'$	119	(3)
1	10^3	$s_+ - s_-$	=	$2h + 2h'$	113	(4)
1	8^3	$s_{++--} - s_{+-}$	=	$J - 2J'$	6.1	(1.5)
1	9^3	$s_+ - s_{+--}$	=	$\frac{4}{3}h + \frac{4}{3}J + \frac{4}{3}J'$	82.6	(2.7)
1	8^3	$s_+ - s_{++--}$	=	$h + J + 2J' + h'$	61.2	(2.2)
1	8^3	$s_{+-} - s_-$	=	$h - 2J + h'$	44	(4)
1	8^3	$s_{++++++--} - s_{++++-++-}$	=	$\frac{1}{2}J + \frac{1}{8}J' + h'$	8.2	(2.2)
0.739	8^3	$s_+ - s_-$	=	$2h + 2h'$	90.2	(4.3)
0.739	8^3	$s_{++--} - s_{+-}$	=	$J - 2J'$	13.7	(2.9)
0.739	8^3	$s_{+-} - s_-$	=	$h - 2J + h'$	10.5	(5.0)
0.739	8^3	$s_{++++++--} - s_{++++-++-}$	=	$\frac{1}{2}J + \frac{1}{8}J' + h'$	19	(3)
0.739	8^3	$s_{+++++-+-} - s_{+++-}$	=	$\frac{1}{2}J' + \frac{1}{2}h'$	6.2	(3.2)
0.739	8^3	$s_{++++-++-} - s_{++---++-}$	=	$\frac{1}{2}h + \frac{1}{2}J' - \frac{1}{4}h'$	18.0	(1.9)

Table 2: This table summarizes the entropy differences per sphere between various pairs of stackings at the densities we studied. The subscript on s is a sequence of σ_i's that is repeated to get the stacking sequence, so + denotes *fcc* , − denotes *hcp* , and the others are less simple stackings (see text).

ρ/ρ_{cp}	N	Δs	$10^5 \times \Delta s/k_B$	
0.739	8^3	$s_n^{fcc} - s_{nn}^{fcc}$	8.3	(1.9)
0.739	8^3	$s_n^{hcp} - s_{nn}^{hcp}$	7.8	(1.9)

Table 3: The entropy differences per sphere between hard sphere crystals with only nearest neighbor interactions (n) and the otherwise identical system with both nearest and next nearest neighbor interactions (nn). The systems with added interactions have lower entropy, but the change is independent of the stacking pattern at the present statistical accuracy.